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THE INFRARED AND RAMAN SPECTRA OF
ISOPROPYLMETHYLPHOSPHONOFUORIDATE (GB)

Harry P. DeLong

Edgewood Arsenal
Edgewood Arsenal, Maryland

January 1973

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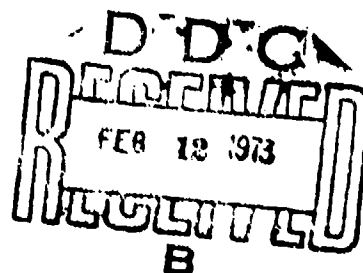
**THE INFRARED AND RAMAN SPECTRA OF
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by

Harry P. DeLong

**Defense Systems Division
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FOREWORD

The work described in this report was authorized under Task 1B622401AD2702, Area Scanning Alarms Techniques. This work was started in June 1971 and completed in December 1971. The experimental data are contained in laboratory notebooks 8500 and 8626.

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DIGEST

Before beginning our experiment, we searched the literature but found no information on the Raman spectrum of isopropylmethylphosphonofluoridate (GB). Thus our presentation on the Raman spectrum is the first. This work is part of an effort to characterize the spectral properties of nerve agents. We compared the data obtained from the Raman spectrum with that obtained from the infrared spectrum; using these data, we made a thorough analysis of vibrational assignments. The information presented here is applicable to the design of specific detection instrumentation for the Remote Raman detection system.

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THE INFRARED AND RAMAN SPECTRA OF ISOPROPYLMETHYLPHOSPHONOFUORIDATE (GB)

I. INTRODUCTION.

This work is part of an in-house and a contractual effort to characterize the spectral properties of nerve agents. One previous report¹ has been written in which the scattering cross sections of several G- and V-type agents were discussed. The infrared (IR) and Raman spectra of liquid isopropylmethylphosphonofluoridate (GB) were recorded. To my knowledge, no previous Raman spectrum of GB is available in the literature.

II. EXPERIMENTATION.

The IR spectrum of GB was obtained by Barrett and Dismukes,* using a Beckman IR-12 infrared spectrophotometer with digital output capabilities. The spectral data were obtained from a magnetic tape containing digitized absorptivity coefficients determined by Barrett and Dismukes.

The sample of GB used for the Raman study was supplied by the Chemical Laboratory of Edgewood Arsenal.

A Raman spectrophotometer, designed and built by Block Engineering, Inc., was used to record the Raman spectrum from 100 to 3100 cm^{-1} . The spectrophotometer consists of an AVCO-pulsed nitrogen laser, wavelength 3371 Å, as the Raman source and a SPEX 1400-II double-pass monochromator. The system was set up for 180° viewing. The monochromator was calibrated using the emission lines from the nitrogen laser. The monochromator alignment was checked daily using the 991.6 cm^{-1} line of benzene. The width of the laser wavelength restricted resolution to one angstrom. This translated to between 7 and 8 wavenumbers (cm^{-1}) resolution over the spectral range. The sample cells are standard silica cuvettes of the type used for UV spectroscopy.

III. RESULTS AND DISCUSSION.

GB falls into symmetry group C_1 . This is a point group without symmetry having only one vibrational mode, A_1 . The molecule has 48 fundamental vibrations; all should be symmetric; and all should be both IR- and Raman-active. The 48 vibrations can be further characterized as 9 fundamentals from the CH_3 , 27 fundamentals from the $\text{CH}(\text{CH}_3)_2$, and 18 skeletal vibrations; all should be below 1350 cm^{-1} . Using the technique of Durig et al.,² the CH_3 vibrations may be assigned as follows: the bands at 2939 cm^{-1} in the IR and at 2942 cm^{-1} in the Raman have significantly different intensities; the Raman band is the more intense. Similarly, the bands at 2986 cm^{-1} in the IR and at 2999 cm^{-1} in the Raman have different intensities, with the IR band

* Private Communication.

¹ DeLong, H. P. EATR 4615. Raman Scattering Cross Sections for Various G and V Agents (U). March 1972. CONFIDENTIAL Report.

² Durig, J. R., Mitchell, B. R., DiYorio, J. S., and Block, F. EATR 4027. Vibrational Spectra of Organophosphorous Compounds II. Vibrational Spectra of CH_3POF_2 and CH_3POFCI . July 1966. UNCLASSIFIED Report.

being the more intense. Since symmetric vibrations are stronger in the Raman than are the antisymmetric and the inverse is true in the IR, it is possible to assign the higher frequency bands to the asymmetric C-H stretch of $-\text{CH}_3$ and the lower frequency bands to the symmetric C-H stretch of $-\text{CH}_3$. The bands at 2880 cm^{-1} (IR) and 2884 cm^{-1} (R) are probably due to the C-H in $\text{CH}(\text{CH}_3)_2$.

The CH deformation for CH_3 probably occurs at 1455 cm^{-1} in the IR and at 1459 cm^{-1} in the Raman, with unresolved bands occurring between 1370 and 1385 cm^{-1} corresponding to the $-\text{CH}(\text{CH}_3)_2$.

The IR spectrum has two absorptions in the 1270 to 1320 cm^{-1} region. The Raman has one moderate band at 1277 cm^{-1} with another weak band at 1323 cm^{-1} . Thomas and Chittenden³ has suggested that the IR band at 1316 cm^{-1} may be due to P-CH_3 . Based on their data, compounds having the general GB structure should have a sharp band of medium intensity in the range of 1313 to 1328 cm^{-1} . There should also be a second band, from medium to strong in intensity, sometimes occurring as a doublet, in the 900 to 934 cm^{-1} region. The results of our examination of the IR spectrum agreed with their predictions. There is a high frequency band at 1316 cm^{-1} and a doublet at 904 and 923 cm^{-1} . The corresponding low frequency band in the Raman may be the band at 930 cm^{-1} . Recently, Mortimer⁴ suggested that organophosphorus compounds of the type $(\text{R-O})_3\text{P=O}$ may have rotational isomers in the liquid state. Their presence is indicated if there are two bands in the P=O region of the spectrum. The existence of rotational isomers has been verified by Nyquist and Muelder^{5,6} and by Durig and DiYorio.⁷ Therefore, there is some question as to whether the 1316 cm^{-1} band in the IR and the 1323 cm^{-1} band in the Raman are the P-CH_3 or the P=O of an isomer of GB.

There are three very distinctive IR bands in the 1090 to 1180 cm^{-1} region that correspond to three bands in the Raman. Thomas and Chittenden⁸ have written that isopropyl phosphorous esters will give three very distinctive bands here. Thus these three bands are assigned to $\text{P-O-CH}(\text{CH}_3)_2$.

In the IR, an intense absorption at 1013 cm^{-1} appears. This is attributed to the P-O-C linkage of GB. Thomas and Chittenden⁸ express a belief that P-O-C falls in the 950 to 1018 cm^{-1} range. The corresponding Raman band is notably very weak. There is some controversy as to whether the band in the 1000 cm^{-1} region is a P-O-C vibration, a C-O vibration, or a P-O

³ Thomas, L. C., and Chittenden, R. A. Characteristic Infra-red Absorption Frequencies of Organophosphorous Compounds-V. *Spectrochim. Acta*, **20**, 1905 (1965).

⁴ Mortimer, F. S. Vibrational Assignment and Rotational Isomerism in Some Simple Organic Phosphates. *Spectrochim. Acta*, **9**, 270 (1957).

⁵ Nyquist, R. A., and Muelder, W. W. An Infrared Study of Organophosphorous Compounds I. *Spectrochim. Acta*, **22**, 1563 (1966).

⁶ Nyquist, R. A. An Infrared and Raman Study of Organophosphorous Compounds-II. *Spectrochim. Acta*, **23A**, 1499 (1967).

⁷ Durig, J. R., and DiYorio, J. S. Vibrational Spectra of Organophosphorous Compounds IV. *J. Chem. Phys.*, **48**, 4154 (1968).

⁸ Thomas, L. C., Chittenden, R. A. Characteristic Infrared Absorption Frequencies of Organophosphorous Compounds II. *Spectrochim. Acta*, **20**, 489 (1964).

vibration.^{5,9} In a recent study by Durig and Clark¹⁰ they expressed the belief that bands at 1036 and 752 cm^{-1} are best characterized by antisymmetric and symmetric stretch vibrations of the molecule $\text{CH}_3\text{-O-PSCl}_2$. An examination of the IR and Raman spectra of GB in this region showed that at 1013 cm^{-1} in the IR there is a strong band, and at 1020 cm^{-1} in the Raman there is a weak band. In the 730 cm^{-1} region (725 cm^{-1} for IR and 727 cm^{-1} for Raman), there is a weak band in the IR and a strong band in the Raman. This alternation of intensities lends credence to the concept of asymmetric and symmetric vibrations. In this case, the higher frequency could be attributed to the asymmetric P-O-C stretch because the IR is the more intense, and the lower frequency vibration would be attributed to the symmetric P-O-C because the Raman band is the more intense.

The P-F stretch occurs in the interval of 810 to 885 cm^{-1} according to Bellamy.¹¹ This is substantiated by Chittenden and Thomas.¹² For the family structure to which GB belongs, the P-F region given by Thomas¹² is 833 to 849 cm^{-1} . Based on this information, the 840 cm^{-1} band in both the IR and the Raman may be assigned to the P-F stretching vibration.

Durig,² in an examination of CH_3POF_2 , assigned an intense band in the 751 cm^{-1} region to P-C. In a study¹³ of CH_3PCl_2 , CH_3POCl_2 , and CH_3PSCl_2 , he assigned bands at 757 cm^{-1} to P-C vibration. In this latter case the bands are of moderate intensity. At present this appears to be a satisfactory, tentative assignment for the 778 cm^{-1} band in the IR and the corresponding Raman band at 781 cm^{-1} .

There is a weak IR band at 509 cm^{-1} and a moderate Raman band at 507 cm^{-1} . These bands and those below 400 cm^{-1} are, for the time being, left unassigned. Durig and Nyquist, reports cited above, are the only persons who have examined the structure of organophosphorous compounds in the low wavenumber region. Unfortunately, their work is only distantly related to our work since they have studied symmetric molecules. Some tentative assignments may be given using their work. The 509 cm^{-1} IR (507 cm^{-1} , Raman) band may be assigned to a P-F symmetric stretch. This is based on Durig's studies^{2,7} of compounds containing two halogens. In studies using deuterated samples, Durig was able to assign the 400 cm^{-1} region to the P-O-C bending vibration. He used very simple molecules containing P-O- CH_3 . In GB, the corresponding band is P-O- $\text{CH}(\text{CH}_3)_2$. Thus the P-O-C band for GB should have a vibration which is near to the P-O- CH_3 . Thus the band at 414 cm^{-1} could be the P-O-C band for GB. Closer to the exciting line there are bands which are probably due to additional P-O-C vibrations, P=O bending, and/or CH_3 torsion. No attempt was made to assign these bands.

Reexamining the higher frequency position, we found two Raman bands in the 2700 cm^{-1} region. Bands in this region imply that there was some phosphonofluoridic acid present as a degradation product.

⁹ Durig, J. R., and DiYorio, J. S. Vibrational Spectra of Organophosphorous Compounds III. *J. Chem. Phys.* **48**, 4154 (1968).

¹⁰ Durig, J. R., and Clark, J. W. Vibrational Spectra and Structure of Organophosphorous Compounds VI. *J. Chem. Phys.* **50**, 107 (1969).

¹¹ Bellamy, L. J. *The Infra-Red Spectra of Complex Molecules*. p 321. Methuen & Co. Ltd. 1958.

¹² Chittenden, R. A., and Thomas, L. C. Characteristic Infrared Absorption Frequencies of Organophosphorous Compounds IV. *Spectrochim. Acta* **21**, 861 (1965).

¹³ Durig, J. R., Block, F., Levin, I. W. Infrared Spectra of CH_3PCl_2 , CH_3POCl_2 , and CH_3PSCl_2 . *Spectrochim. Acta* **21**, 1105 (1965).

The table lists the IR and the Raman band positions. Both band intensities are given on a relative scale to the most intense band in the spectrum. The Raman and the IR spectra are given in the figure.

Table. Infrared and Raman Spectra of GB

Infrared Spectrum	Relative Intensity	Raman Spectrum	Relative Intensity	Assignments
cm ⁻¹		cm ⁻¹		
		3033	60.30	
2986	11.6	2999	66.25	CH ₃ antisymmetric stretch
2939	3.79	2942	100.00	CH ₃ symmetric stretch
2880	1.44	2884	37.4	CH stretch
1468	3.53			CH bend
1455	2.88	1459	43.1	CH ₃ bend
1418	3.26	1427	33.4	
1387	8.65	1395	25.7	CH(CH ₃) ₂
1377	7.42			
1357	4.64	1357	30.5	
1316	39.5	1323	24.1	P=O or CH ₃ -P asymmetric stretch
1284	42.1	1277	42.8	P-O
1179	4.21	1184	22.5	
1144	6.13	1148	24.6	O-CH(CH ₃) ₂
1105	9.57	1108	28.8	
1013	100.	1020	20.5	P-O-C asymmetric stretch
923	28.2	930	22.8	
904	18.9			
883	3.80	886	34.0	
840	28.6	840	20.8	P-F asymmetric stretch
778	7.42	781	28.5	P-C stretch
725	8.10	727	100.0	P-O-C symmetric stretch
509	8.28	507	42.1	P-F symmetric stretch
		414	25.9	
		316	25.8	
		279	37.8	
		260	43.4	
		214	24.0	
		153	27.4	

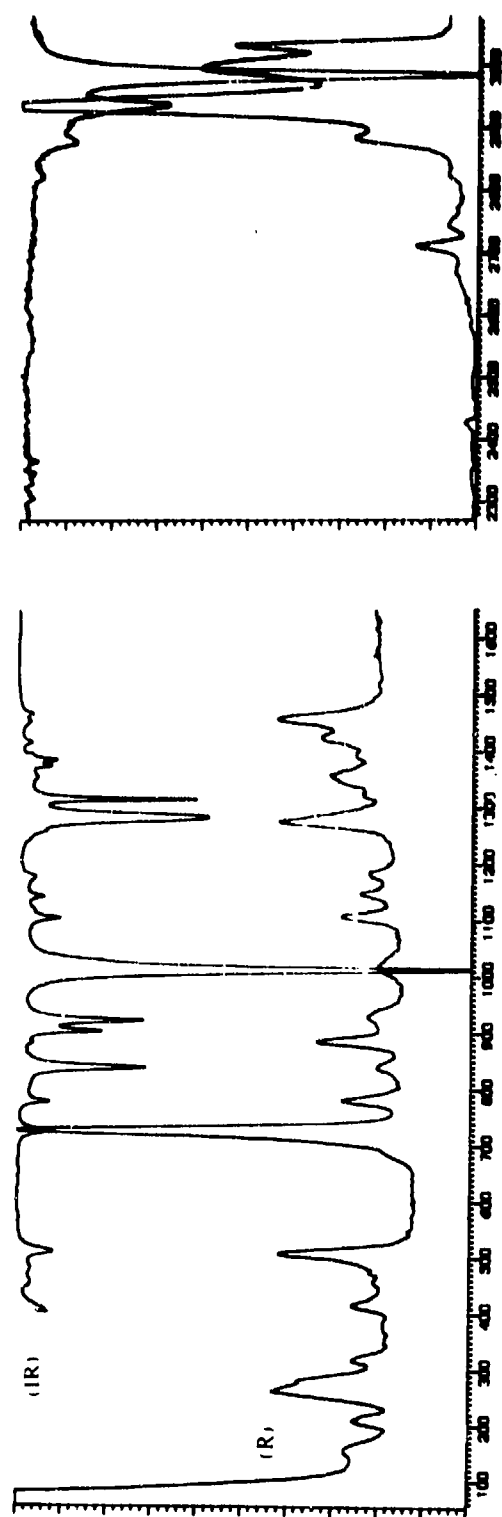


Figure. Infrared (IR) and Raman (R) Spectra

IV. CONCLUSIONS.

The Raman spectrum of GB has been presented for the first time in the literature. Using this data, a thorough examination of the vibrational assignments has been made. The majority of the bands have been identified. Data have been presented which substantiates the concept of a symmetric and asymmetric P-O-C stretch vibration in the 700 and 1000 cm^{-1} regions. This finding is contrary to earlier assignments of bands in these two regions, P-O and C-O, respectively.

Several bands remain unassigned. These lie in the low wavenumber region. Until far-IR spectra become available on the various G-type compounds, or on similar compounds, their identity must remain unknown. Also, as more Raman data become available in this region, there is a possibility that various correlations may be established.

In the higher wavenumber region, the question about the identity of the two bands in the 1300 cm^{-1} region must likely await low temperature studies. As Mortimer,⁴ Durig,⁷ and Nyquist⁵ have demonstrated, various isomers may be examined by observing band intensity variation with temperature. Using such a procedure it is possible to determine which bands are due to which isomer.

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